Vapor-phase Diffusion of Benzene in Soil*

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ABSTRACT

The volatilization of benzene (C,H,), a component of volatile emissions from landfills receiving certain industrial wastes, was characterized in the laboratory using a simulated landfill apparatus. The steady-state vapor diffusion of C,H, in soil under isothermal conditions and negligible water flow was directly related to soil air-filled porosity. The volatilization flux of C,HI through a soil cover was greatly reduced by increased soil bulk density and increased soil-water content. The actual flux through the soii cover could be predicted from the soil porosity term, $Pi'''P;'$, where P_a is the soil air-filled porosity and P_t is the total porosity. The diffusion coefficient in air for C_6H_6 calculated from the experimental results was $8.91 \times 10^{-6} m^2 s^{-1}$, at 2O"c, which agrees with other reported data.

Additional Index Words: volatilization, landfills, industrial wastes, air-filled porosity, soil bulk density, soil-water content.

Disposal of toxic substances on land has led to concern over air pollution due to the emission of volatile and semivolatile organics from the surface of landfills. Analysis of air samples near a Class I landfill site has revealed the presence of such organics as benzene (GH,), vinyl chloride, chloroform, trichloroethane, toluene, tetrachloroethylene, etc. (Karimi, 1983). Emissions of this type have been known to contribute to photochemical smog and nuisance odor (Kohei et al., 1982). Industrial wastes containing these and other highly volatile substances, once disposed of in a landfill, can be transported to the soil surface where they will be subject to volatilization into the atmosphere. Depending on the relative values of certain physical and chemical properties, such as vapor pressure and water solubility of a particular compound, vapor-phase diffusion can be a major transport mechanism for controlling movement through a soil cover to the atmosphere (Jury et al., 1984).

An understanding of the effects of soil parameters on vapor-phase transport is essential.

Published data on the volatilization of most industrial wastes from soil covering a landfill is limited. In particular, information is limited on the volatilization from soil of compounds of low molecular weight such as C_6H_6. There is a considerable body of information in the literature on the volatilization from soil of compounds of intermediate vapor pressure such as pesticides and other toxic organic compounds (Spencer and Farmer, 1980). Farmer et al. (1980b) presented a method of estimating the volatilization rate of hexachlorobenzene-containing wastes from landfills based on vapor-phase diffusion through soil as the controlling transport mechanism.

The extent to which vapor-phase diffusion occurs in a soil will depend on the air-filled porosity of that soil. Air-filled porosity, in turn, is determined in part by soil bulk density and soil-water content. Molecular diffusion in a soil is not generally related in a strictly linear fashion to air-filled porosity but is modified by the tortuosity of the soil pores. The model of Millington and Quirk (1961) has been used to account for the effects of soil porosity on the diffusion of moderate to low volatile organic compounds in soil (Shearer et al., 1973; Farmer et al., 1980a). Little research has been reported on the influence of soil porosity on the vapor-phase transport of low molecular weight compounds characteristic of volatile emissions from landfills.

In the present study C_6H_6 was selected as a volatile organic compound typical of compounds most frequently emitted from a land disposal site. Thus, C_6H_6 became the focus of further laboratory investigations. The objective of this paper is to evaluate soil parameters such as bulk density, water content, and air-filled porosity for their influence on describing steady-state vapor diffusion of C_6H_6 in soil. For this purpose a simulated landfill study was carried out under controlled laboratory conditions.

THEORY

The steady-state flux of a volatile organic compound through a soil cover of depth L, as depicted in the volatilization cell shown in Fig. 1, can be approximated by Fick's first law and can be expressed as

$$J = -D_s (C_a - C_s)/L \qquad [1]$$

where

J = vapor flux through the soil (kg $m^{-2} s^{-1}$),

D_s = apparent steady-state vapor diffusion coefficient ($m^2 s^{-1}$),

C_2 = concentration in the air at the surface of the soil (kg m^{-3}),

C_s = concentration in the air at depth L (kg m^{-3}), and

L = depth of the soil layer (m).

Although air-filled porosity has been found to be the major soil parameter controlling volatilization flux through a soil-water-air system, the apparent steady-state vapor diffusion coefficient depends not only on the amount of air-filled pore space but also on the nature of the soil tortuosity. it has been pointed out (Shearer et al., 1966) that in adding liquid to a porous system, there was a much greater reduction in the apparent gas diffusion coefficient than could be accounted for by the reduction in gas-filled pore volume by the addition of the liquid and the resultant closer packing of the solid and liquid phases. The presence of liquid films on the solid surface not only reduces the porosity but also modifies the pore geometry and the length of the gas passage. Thus, the apparent gas diffusion coefficient through a porous medium is clearly a function of both internal geometry and porosity. Millington and Quirk (1961) suggested an apparent vapor diffusion coefficient that includes a porosity term to account for the geometric effects of the soil system. Based on a theoretical derivation, they presented a model for the apparent vapor diffusion coefficient including air-filled porosity and the total porosity of the soil system. Shearer et al. (1973) successfully used the apparent vapor diffusion coefficient model suggested by Millington and Quirk to compute the apparent vapor phase diffusion coefficient of a pesticide (lindane (I ,2,3,4,5,6-hexachlorocyclohexane]) in soil.

According to Millington and Quirk (1961), the apparent vapor diffusion coefficient can be expressed as

$$D_s = D_a (P_a^{10/3}/P_T^2) \qquad [2]$$

where

D_a = vapor diffusion coefficient in air ($m^2 s^{-1}$),

P_a = air-filled porosity ($m^3 m^{-3}$), and

P_T = total porosity ($m^3 m^{-3}$).

There is an additional effect of the presence of soil particles and of the presence of liquid films on the solid surfaces. Interactions between the compound and adsorption sites on the soil surface and solubility in the liquid film will temporarily reduce the vapor-phase concentration and therefore reduce diffusion in the gas phase. This reduction in vapor-phase concentration will influence the time required for the system to reach steady state. However, once all adsorption sites are satisfied, the final apparent steady-state vapor-diffusion coefficient will be determined by the air-filled porosity and not by the ability of the soil matrix to retain the organic compound. As the soil-water content changes or with soils with varying adsorption capacity, e.g., higher organic C content, the length of time required to achieve steady state will vary.

MATERIALS AND METHODS

Soil Characteristics and Preparation

Soils from the surface to about the IO-cm depth were collected from the BKK landfill in West Covina, CA, a site that has been used for disposal of industrial wastes. The soil samples were collected directly from a landfill cover and used for experimental diffusion measurements. Additional samples were taken for field bulk density measurements. The soil for the diffusion experiments was sieved to 2 mm and thoroughly mixed prior to use. Soil texture and soil organic matter content were determined using the hydrometer method (Day, 1965) and the Walkley-Black method (Allison, 1965), respectively. For the determination of soil parti-
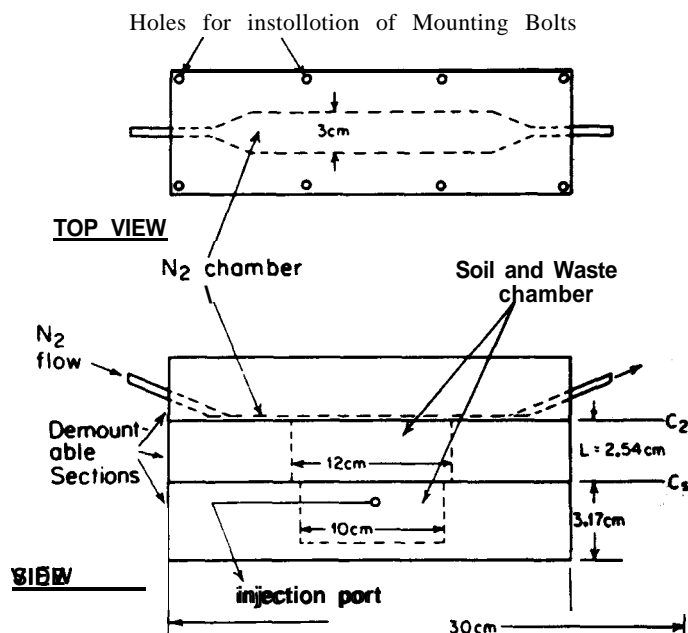

Fig. 1. Details of volatilization cell used in simulated landfill studies.

cle density, six sampler were analyzed using the method described by Blake (1965). The results of soil particle density measurements were calculated at a 99% confidence level and found to be 2.80 ± 0.27 Mg m^{-3}. The field bulk density of the soil collected for laboratory study was found to be 1.16 M_{LR} m^{-3} with a pH of 7.U (3:1, H_2O/soil). The texture of the soil was determined to be day, with 54% clay and 46% silt and fine sands. This soil contained 7.3 g kg^{-1} organic matter.

For the landfill simulation experiments, soil-water contents ranging from 0.086 ± 0.012 to 0.113 ± 0.008 kg kg-' were prepared by atomizing water onto several kilograms of soil in a S-L glass carboy (Spencer and Cliath, 1969). The soil was turned frequently during the atomizing step to obtain uniform water content. The soil was equilibrated in the carboy for 72 h at 20°C in a constant temperature chamber before being used in the volatilization experiments.

Simulated Landfill (Volatilization Cell)

Figure 1 shows details of the volatilization cell that was used to measure the steady-state diffusion of C_6H_6 through a soil cover. The cell, a modification of a previously reported volatilization cell (Farmer et al., 1980a; Spencer and Cliath, 1979), was designed to accommodate a liquid, such as C_6H_6, with or without a soil cover. The cell was constructed of Al in order to resist corrosion. The cell consisted of a rectangular waste chamber 3-cm wide by IO-cm long. The depth of the cell was variable through the stacking of additional center sections to accommodate various waste layers and coverings. For these experiments a soil chamber depth of 2.54 cm was used. One centimeter was added to each side and to each end of the length and width of the central soil chamber beyond that of the waste and vapor chambers to minimize wall effects on the movement of C_6H_6 molecules. Each section was grooved for an O ring to provide a positive liquid and vapor seal between sections. Provisions were made to allow each section to be individually sealed in place and filled to a predetermined volume or level before the next section was added. The upper section contained a vapor chamber 2-mm deep and 3-cm wide through which N_2 gas was allowed to flow to carry away any volatilized C_6H_6. The vapor chamber extended 7.5 cm on either side of the sample chamber to allow the N_2 gas to spread before reaching the soil surface, thus providing laminar flow across the central chamber. A small port was provided on the side wall of the bottom waste chamber in order to inject C_6H_6 under the soil cover by means of a syringe. The C_6H_6
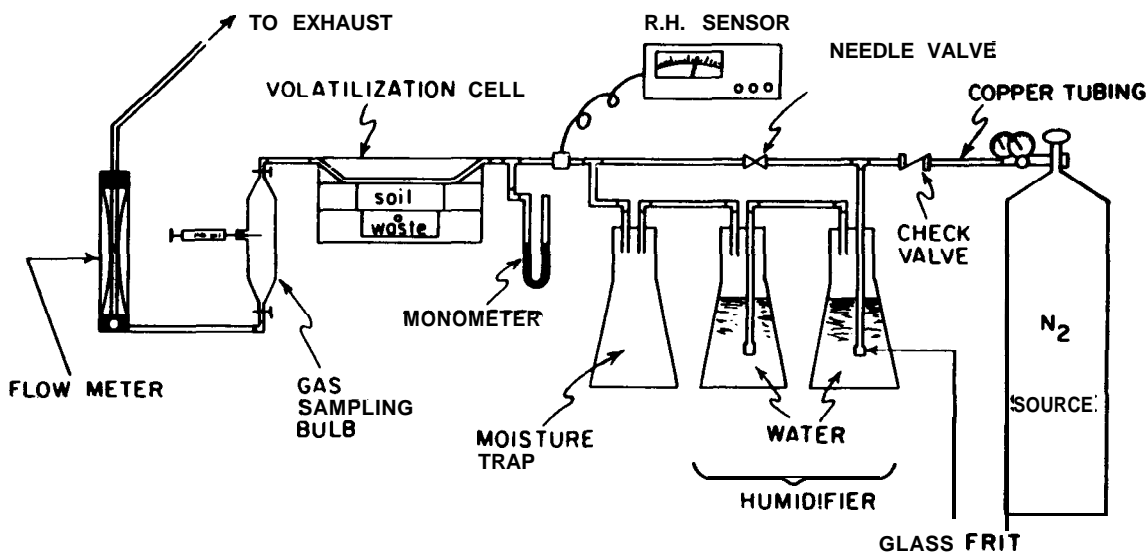
Fig. 2. Schematic diagram of closed flow system for collecting volatilized organic compounds from a simulated landfill operation (not drawn to scale).

formed a liquid layer on the bottom of the waste chamber. After placement of the C_6H_6, the port was sealed by a screw and Teflon washer.

Vapor Loss Rate Studies

Figure 2 depicts a schematic of the volatilization measurement system for the simulated landfill. The rate of C_6H_6 volatilization (flux) from the soil surface was measured in a closed system by collecting samples of volatilized chemical from a gas bulb via a gas-tight syringe. The tubing consisted of Cu with a o.d. of 7 mm. The entire apparatus was maintained inside a walk-in constant temperature chamber. The relative humidity of the N_2 gas used to simulate air was adjusted to 60% by passing a portion of the incoming N_2 flow through a humidifier. This relative humidity represents an average value that might be expected in a natural environment, recognizing that wide fluctuations are common. The temperature of the chamber remained at 20°C. The rate of C_6H_6 volatilization from soil was measured at various soil bulk densities

Table 1. Summary of variables used and the steady-state C_6H_6 vapor densities measured for the volatilization studies.

Experiment no.	Bulk density	Soil-water content	Average soil-water contents	Vapor† density ($\times 10^{-3}$)
	Mg m⁻³	——— kg kg⁻¹ ———		kg m⁻³
1	1.1	0.111		6.15
2	1.25	0.113		3.63
3	1.44	0.116	0.113	2.25
4				
5	1.48 1.61	0.108 0.119		2.10 1.42
6	1.21	0.076		5.74
7				
8	1.23 1.27	0.086 0.068	0.086	4.12 4.26
9	1.39	0.086		3.18
10	1.52	0.092		2.13
11	1.15	0.089		4.98
12	1.26	0.082		4.33
13	1.30	0.067	0.086	3.60
14	1.38	0.085		2.81
15	1.48	0.089		2.64
16	1.20	0.096		4.58
17	1.27	0.104		3.84
18	1.38	0.103	0.102	3.51
19	1.40	0.110		3.16
20	1.64	0.096		1.62

† The steady-state C.H. vapor densities for C_6H_6 volatilizing from soil were determined at 20 °C and a N, flow rate of 16.7 mL s⁻¹.

and soil-water contents. The C_6H_6 volatilization experiments carried out in this study are summarized in Table 1.

In C_6H_6 volatilization experiments, sufficient soil, previously equilibrated to a given water content, was weighed to yield the desired bulk density and packed into the soil chamber. The soil layer was retained in place in the soil chamber by means of a fine mesh stainless steel screen placed beneath the soil layer. A manometer was installed near the entrance of the volatilization cell. The pressure of the system was adjusted to minimize any differential between the N_2 flowing through the cell and the atmosphere, which could interfere with the natural diffusion process. The packing and assembly of the cell was performed in the constant temperature chamber of 20°C. The assembled cell was connected to a closed N_2 flow system and N_2 flow was adjusted to 16.7 mL s⁻¹(1.0 L min⁻¹). This flow rate exchanged the N_2 gas within the vapor chamber above the soil surface 167 times min⁻¹. Fifteen milliliters of C_6H_6 was then injected into the bottom section of the cell via the injection port. A vapor gap between the C_6H_6 layer and the soil surface prevented the C_6H_6 from migrating by liquid flow through the soil. The C_6H_6 emitted from the soil surface was sampled from the gas sampling bulb at 5-min intervals by a gas-tight syringe and analyzed by gas chromatography. The volume of the gas sampling bulk was approximately 200 mL. At a N_2 flow rate of 16.7 mL s⁻¹ this would result in the N_2 being exchanged in the sampling bulb approximately 10 times min⁻¹. Soil-water contents were determined at the beginning and end of each volatilization experiment. The final soil-water content varied only slightly from initial values even though 60% relative humidity was used. This was primarily due to the short time periods required for each experiment. The final soil-water contents, as reported in Table 1, were used in calculating soil porosity values. The final values were considered to be most characteristic of final steady-state C_6H_6 flux.

Gas Chromatographic Analysis of Benzene

The collected gas samples from the volatilization experiments were analyzed by gas chromatography (GC) with a flame ionization detector (FID). Sample sizes varied from 20 to 500 µL, depending on the C_6H_6 concentration. The detection limit for C_6H_6 was 0.1 mg m⁻³. Standard C_6H_6 in air with a concentration of 0.386 g m⁻³ ± 2% was obtained from Scott Environmental Technology, Inc. (San Bernardino, CA).

RESULTS AND DISCUSSION

Benzene Saturation Vapor Density

The C_6H_6 saturation vapor density from spectro-quality grade C_6H_6 at 20°C temperature was measured by
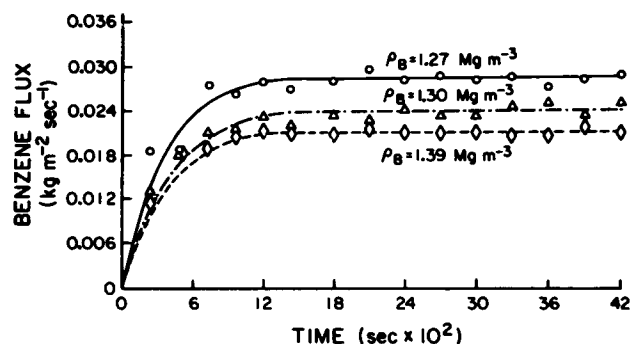
Fig. 3. Effect of soil bulk density on the volatilization of C_6H_6 covered with a 2.54-cm soil cover. Final soil-water contents varied from 8.56 to 8.70% (Exp. no. 8, 9, and 13).

Fig. 4. Effect of soil bulk density, ϱ_b, on the specific C_6H_6 volatilization flux through a 2.54-cm soil cover with 11.30 ± 0.82% water content (Exp. no. 1, 2, 3, 4, and 5).

headspace analysis as 0.318 kg m^{-3}. This value is fairly close to the value of 0.322 kg m^{-3} reported in the literature (Riddick and Bunger, 1970).

Volatilization from Simulated Landfill with a Soil Cover

Representative volatilization flux data for C_6H_6 covered with 2.54-cm soil are shown in Fig. 3. The flux increases rapidly and reaches steady state in 30 min or less. The rapid emergence of C_6H_6 at the soil surface indicates that adsorption of C_6H_6 by the soil matrix is not significant. Using the example of the lower flux curve in Fig. 3, the fact that the flux reaches a steady-state value of 1.26 kg m^{-2} min^{-1} after 30 min indicates that there is no additional adsorption of C_6H_6 taking place by the soil after this time. Since there was no contact between the liquid C_6H_6 and the cover soil, all the flux can be attributed to diffusion. There was no mass flow of C_6H_6 due to capillary transport.

Benzene may move by molecular diffusion in soil in the vapor phase and in the solution phase. The relative importance of vapor-phase and solution-phase diffusion is determined by the relative magnitude of the concentration in air (vapor density) and the concentration in solution phase (Goring, 1962; Letey and Farmer, 1974). Chemicals with partition coefficients between the soil water/soil air $\ll 10^4$ will diffuse mainly in the vapor phase and those with partition coefficients $\gg 10^4$ will diffuse primarily in the solution phase (Goring, 1962; Letey and Farmer, 1974; Farmer et al., 180a). The C_6H_6 solubility in water at 25 °C is 0.18% (Haxo et al., 1977), and the vapor density at 25 °C is 0.390 kg m^{-3}. This yields a partition coefficient of 4.6 at 25 °C. Therefore, C_6H_6 would be expected to diffuse primarily in the vapor phase.

The effect of soil bulk density, soil-water content, and the resulting soil porosity on the vapor phase diffusion of C_6H_6 in soil was evaluated. Table 1 illustrates the steady-state vapor densities measured for C_6H_6 volatilizing from the soil cover at different soil bulk densities and soil-water contents. Since soil bulk density and soil-water content are both soil characteristics that can be altered directly as practical measures to effect a change in vapor flux, the two factors are considered separately in the following sections before the overall effect of changes in porosity are considered.
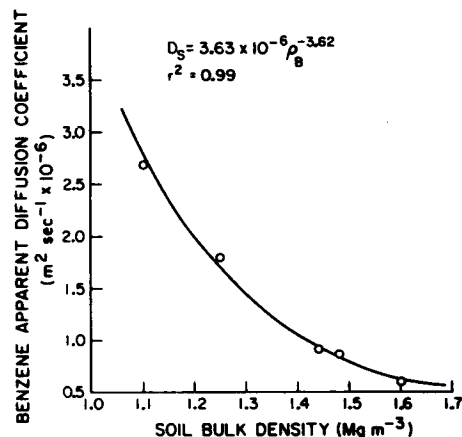
Soil Bulk Density

When C_6H_6 or C_6H_6-containing waste is covered with soil, the type of soil used and the amount of pressure applied to compact the soil will affect the degree of compaction. Soil compaction, and consequently its bulk density, determines the total porosity of a soil and, thus, affects C_6H_6 vapor diffusion through the soil. Benzene volatilization fluxes through a 2.54-cm soil cover at various bulk densities and nearly identical soil-water contents (wt/wt) are shown in Fig. 3. Compaction of the C_6H_6 fluxes show that C_6H_6 volatilization through a soil cover of lower bulk density are greater than those through a soil cover of higher bulk density. Since the final soil-water contents are very close to one another and all of the soil covers are of the same thickness, the difference in C_6H_6 volatilization can be attributed to the influence of soil bulk densities on the soil air-filled porosity.

The quantitative effect of soil bulk density on C_6H_6 volatilization flux through a soil cover can be observed by plotting the apparent steady-state C_6H_6 diffusion coefficient from Eq. [1] against the soil bulk density (Fig. 4). For this purpose, the vapor flux, J, was estimated using the vapor density values at various soil bulk densities from Table 1, the N_2 flow rate of 16.7 mL s^{-1}, and the soil surface area exposed in the volatilization cell. The C_6H_6 vapor concentration measured using the volatilization cell is the average concentration in the air above the soil surface and is assumed to be equivalent to C_2, the C_6H_6 vapor concentration at the soil surface. Since C_s is $\gg$ C_2, the error involved in using this assumption to measure D_s is expected to be small. The concentration, C_s, in the gas phase at depth L, the bottom of the soil layer, is assumed to be equal to that of the saturation vapor density of C_6H_6. This may not be exactly true since a finite time will be required for the C_6H_6 to move from the liquid C_6H_6 surface in the waste chamber to the soil layer. The error in this assumption is expected to be small because movement of C_6H_6 via diffusion in the waste application compartment is much more rapid than diffusion through the soil cover. The soil depth, L, was 2.54 cm in all experiments. At the maximum volatilization flux represented by Exp. 1 in Table 1, the N_2 carrier gas was approximately 2% saturated with C_6H_6 based on the
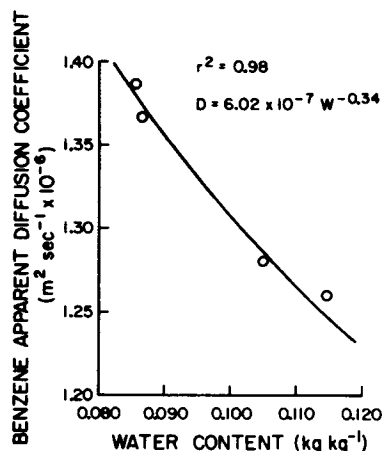
Fig. 5. Effect of soil-water content (wt/wt), W, on the specific C_6H_6 volatilization flux trough a 2.54-cm soil cover with a bulk density of 1.4 Mg m^{-3}.

Fig. 6. Effect of air-filled porosity on the specific C_6H_6 volatilization through a 2.54-cm soil cover.

saturation vapor density value for C_6H_6 of 0.318 kg m^{-3} at 20°C. Thus vapor loss rates for C_6H_6 could be even higher under field conditions where higher gas exchange rates could take place. However, a higher volatilization flux rate due to a greater gas exchange rate would not influence the diffusion coefficient. Theoretically, if the flux rate increased in the volatilization cell due to a greater gas exchange, the value of C_2, the concentration of C_6H_6 in the atmosphere above the soil surface, would decrease allowing D_s to remain unchanged.

Comparison of the apparent steady-state C_6H_6 diffusion coefficients in Fig. 4 shows that decreasing the bulk density from 1.6 to 1.1 Mg m^{-3} increases the steady-state C_6H_6 specific flux by 78% at a soil-water content of 0.113 kg kg^{-1}. Thus, the soil bulk density has an exponential effect ($r^2 = 0.99$) on C_6H_6 volatilization flux through the soil cover. Similar exponential effects of soil bulk density on vapor-phase diffusion flux have been found for hexachlorobenzene (HCB) (Farmer et al., 1980a) and for lindane (Ehlers et al., 1969). It is obvious that higher soil bulk densities result in lower steady-state C_6H_6 flux rates. However, for any given soil there is a limit to the maximum bulk density that can be reached and there will always be a finite amount of open space for vapor diffusion to take place.

Soil-water Content

It is common practice when wastes are being covered with soil to spray water over the soil as a dust control measure and as an aid to obtain maximum compaction of the soil. In addition, the amount of water added to a soil decreases the air-filled pore space available for C_6H_6 vapor diffusion and, thus, affects the C_6H_6 volatilization flux through the soil cover. Figure 5 shows the exponential relationship ($r^2 = 0.98$) between the soil-water content and the apparent steady-state C_6H_6 diffusion coefficient derived from the vapor density data in Table 1. To arrive at this relationship, an exponential relationship was derived between bulk density and D_s for each of the four groups of experiments shown in Table 1, similar to the relationship shown in Fig. 4. From this the D_s at a bulk density of 1.4 Mg m^{-3} was selected and plotted vs.
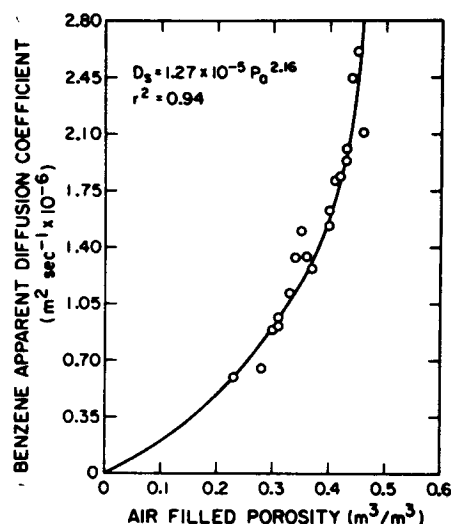
the average soil-water content for that group of water contents. The resulting exponential relationship is shown in Fig. 5. It is clear that steady-state C_6H_6 volatilization flux through a 2.54-cm soil cover with a water content of 0.090 kg kg^{-1} is higher (about 7%) than that through a soil cover of 0.110 kg kg^{-1} water content. Since all four soil covers had similar bulk densities and the same thickness, the difference in C_6H_6 flux must have been caused by the difference in water contents.

Farmer et al. (1980a) studied HCB diffusion in soil and observed a similar effect of soil-water content on vapor phase diffusion. Shearer et al. (1973) also found the same results for lindane. Increasing soil-water content decreases the pore space available for C_6H_6 vapor diffusion and will decrease C_6H_6 volatilization flux. When the soil is saturated with water, it will exhibit the same effect as a covering of water. Soil-water content will exhibit an additional effect on vapor-phase diffusion. By virtue of the solubility of C_6H_6 in water, increasing the soil-water content will increase the capacity of the soil to retain C_6H_6 in the solution phase reducing the quantity of C_6H_6 available for vapor-phase diffusion. Increasing soil-water content will decrease the rate at which steady-state volatilization flux is attained. However, once the solubility of C_6H_6 in soil water is reached, the final steady-state flux will depend on the air-filled porosity and not on the ability of the soil or soil water to adsorb C_6H_6.

Air-filled porosity

Theoretical analysis and experimental results show that vapor-phase diffusion is the major mode of C_6H_6 movement through unsaturated soil. Benzene molecules will have to diffuse through the air-filled pore space of the soil. Thus, the effects of soil-water content and soil bulk density on C_6H_6 volatilization flux through a soil cover can be attributed to their effect on the air-filled porosity, which in turn is the major soil parameter controlling C_6H_6 volatilization through soil. *Air-filled porosity* is defined as that portion of the total soil volume not occupied by either solid soil particles or by soil water. It
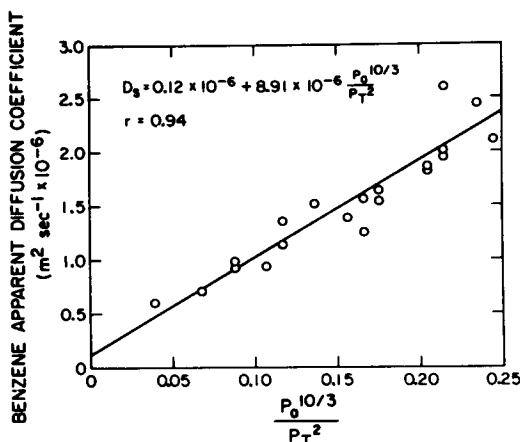
Fig. 7. Linear regression for the relationship between the specific volatilization flux and the ratio $P_a^{10/3}/P_T^2$.

is determined by subtracting the volumetric water content from the total soil porosity, the latter term being a function of the density of the individual soil particles.

Figure 6 shows the effect of air-filled porosity on steady-state C_6H_6 volatilization flux through a 2.54-cm soil cover. Comparison of the different values show that increasing the relative air-filled porosity by 10% increases the apparent steady-state specific C_6H_6 diffusion coefficient 23%, indicating that air-filled porosity has an exponential effect on C_6H_6 volatilization flux through soil. This is a useful relationship. However, a more useful relationhsip results when the soil porosity term of Millington and Quirk (Eq. [2]) is used as presented in the next section.

Determination of Diffusion Coefficient

From Eq. [2] the diffusion coefficient D_o can be determined by plotting D_s vs. ($P_a^{10/3} P_T^{-2}$), and the slope of the linear regression line would be the value of D_o. Figure 7 shows the experimentally determined linear regression line $D_s = 0.12 \times 10^{-6} + 8.91 \times 10^{-6} (P_a^{10/3} P_T^{-2})$, and the corresponding C_6H_6 vapor diffusion coefficient in N_2 is found to be 8.9×10^{-6} m^2 s^{-1}. This value is close to that reported by Thibodeaux (1981) of 8.8×10^{-6} m^2 s^{-1}. The line in Fig. 7 is the best fit line through the experimental data ($r = 0.94$). A statistical analysis of the data shows that the positive y-intercept of Fig. 7 is not statistically different from a zero intercept. A zero intercept is predicted by Eq. [2]. The close fit of the data suggests that Eq. [2] can be used to reasonably estimate vapor diffusion at air-filled porosities >0.2 m^3 m^{-1}.

Application to Landfill Cover Design

The results of this study demonstrate the applicability of the soil porosity term, $P_a^{10/3}/P_T^L$, to predicting the diffusion in porous media of low molecular weight compounds like C_6H_6. For volatile compounds where vapor-phase diffusion can be a dominant transport mechanism, Eq. [1] can be used to assess the effect of altering the air-filled porosity of a soil cover on the volatilization flux of the compound from an industrial waste in a landfill.

For this purpose, Eq. [1] can be simplified by assuming C_2 to be zero (compared to C_s, C_2 is very small). Therefore, Eq. [1] can be written as

$$J = D_s \, C_s / L. \qquad [3]$$

For determination of C_s, it is advised to use the headspace method. In this method a certain amount of waste is brought to equilibrium with its vapor phase, and the vapor phase is analyzed for the contaminant of intereest. Thus D_s is calculated using the estimated D_o and cover soil porosities (Eq. [2]). Equation (3) can also be used to design a soil cover depth in order to reduce the flux to a specified value (Farmer et al., 1980b).

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